
WAC 296-62-07336 Acrylonitrile.

(1) **Scope and application.**

- (a) This section applies to all occupational exposure to acrylonitrile (AN), Chemical Abstracts Service Registry No. 000107131, except as provided in (b) and (c) of this subsection.
- (b) This section does not apply to exposures which result solely from the processing, use, and handling of the following materials:
 - (i) ABS resins, SAN resins, nitrile barrier resins, solid nitrile elastomers, and acrylic and modacrylic fibers, when these listed materials are in the form of finished polymers, and products fabricated from such finished polymers;
 - (ii) Materials made from and/or containing AN for which objective data is reasonably relied upon to demonstrate that the material is not capable of releasing AN in airborne concentrations in excess of 1 ppm as an eight-hour time-weighted average, under the expected conditions of processing, use, and handling which will cause the greatest possible release; and
 - (iii) Solid materials made from and/or containing AN which will not be heated above 170°F during handling, use, or processing.
- (c) An employer relying upon exemption under (1)(b)(ii) shall maintain records of the objective data supporting that exemption, and of the basis of the employer's reliance on the data as provided in subsection (17) of this section.

(2) **Definitions**, as applicable to this section:

- (a) **“Acrylonitrile” or “AN”** - acrylonitrile monomer, chemical formula $\text{CH}_2 = \text{CHCN}$.
- (b) **“Action level”** - a concentration of AN of 1 ppm as an eight-hour time-weighted average.
- (c) **“Authorized person”** - any person specifically authorized by the employer whose duties require the person to enter a regulated area, or any person entering such an area as a designated representative of employees for the purpose of exercising the opportunity to observe monitoring procedures under subsection (18) of this section.
- (d) **“Decontamination”** means treatment of materials and surfaces by water washdown, ventilation, or other means, to assure that the materials will not expose employees to airborne concentrations of AN above 1 ppm as an eight-hour time-weighted average.
- (e) **“Director”** - the director of labor and industries, or his authorized representative.
- (f) **“Emergency”** - any occurrence such as, but not limited to, equipment failure, rupture of containers, or failure of control equipment, which is likely to, or does, result in unexpected exposure to AN in excess of the ceiling limit.
- (g) **“Liquid AN”** means AN monomer in liquid form, and liquid or semiliquid polymer intermediates, including slurries, suspensions, emulsions, and solutions, produced during the polymerization of AN.
- (h) **“Polyacrylonitrile” or “PAN”** - polyacrylonitrile homopolymers or copolymers, except for materials as exempted under subsection (1)(b) of this section.

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(3) Permissible exposure limits.

- (a) Inhalation.
 - (i) Time-weighted average limit (TWA). The employer shall assure that no employee is exposed to an airborne concentration of acrylonitrile in excess of two parts acrylonitrile per million parts of air (2 ppm), as an eight-hour time-weighted average.
 - (ii) Ceiling limit. The employer shall assure that no employee is exposed to an airborne concentration of acrylonitrile in excess of 10 ppm as averaged over any fifteen-minute period during the working day.
- (b) Dermal and eye exposure. The employer shall assure that no employee is exposed to skin contact or eye contact with liquid AN or PAN.

(4) Notification of use and emergencies.

- (a) Use. Within ten days of the effective date of this standard, or within fifteen days following the introduction of AN into the workplace, every employer shall report, unless he has done so pursuant to the emergency temporary standard, the following information to the director for each such workplace:
 - (i) The address and location of each workplace in which AN is present;
 - (ii) A brief description of each process of operation which may result in employee exposure to AN;
 - (iii) The number of employees engaged in each process or operation who may be exposed to AN and an estimate of the frequency and degree of exposure that occurs; and
 - (iv) A brief description of the employer's safety and health program as it relates to limitation of employee exposure to AN. Whenever there has been a significant change in the information required by this subsection, the employer shall promptly amend such information previously provided to the director.
- (b) Emergencies and remedial action. Emergencies, and the facts obtainable at that time, shall be reported within 24 hours of the initial occurrence to the director. Upon request of the director, the employer shall submit additional information in writing relevant to the nature and extent of employee exposures and measures taken to prevent future emergencies of a similar nature.

(5) Exposure monitoring.

- (a) General.
 - (i) Determinations of airborne exposure levels shall be made from air samples that are representative of each employee's exposure to AN over an eight-hour period.
 - (ii) For the purposes of this section, employee exposure is that which would occur if the employee were not using a respirator.

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- (b) Initial monitoring. Each employer who has a place of employment in which AN is present shall monitor each such workplace and work operation to accurately determine the airborne concentrations of AN to which employees may be exposed. Such monitoring may be done on a representative basis, provided that the employer can demonstrate that the determinations are representative of employee exposures.
- (c) Frequency.
 - (i) If the monitoring required by this section reveals employee exposure to be below the action level, the employer may discontinue monitoring for that employee. The employer shall continue these quarterly measurements until at least two consecutive measurements taken at least seven days apart, are below the action level, and thereafter the employer may discontinue monitoring for that employee.
 - (ii) If the monitoring required by this section reveals employee exposure to be at or above the action level but below the permissible exposure limits, the employer shall repeat such monitoring for each such employee at least quarterly.
 - (iii) If the monitoring required by this section reveals employee exposure to be in excess of the permissible exposure limits, the employer shall repeat these determinations for each such employee at least monthly. The employer shall continue these monthly measurements until at least two consecutive measurements, taken at least seven days apart, are below the permissible exposure limits, and thereafter the employer shall monitor at least quarterly.
- (d) Additional monitoring. Whenever there has been a production, process, control or personnel change which may result in new or additional exposure to AN, or whenever the employer has any other reason to suspect a change which may result in new or additional exposures to AN, additional monitoring which complies with this subsection shall be conducted.
- (e) Employee notification.
 - (i) Within five working days after the receipt of monitoring results, the employer shall notify each employee in writing of the results which represent that employee's exposure.
 - (ii) Whenever the results indicate that the representative employee exposure exceeds the permissible exposure limits, the employer shall include in the written notice a statement that the permissible exposure limits were exceeded and a description of the corrective action being taken to reduce exposure to or below the permissible exposure limits.
- (f) Accuracy of measurement. The method of measurement of employee exposures shall be accurate, to a confidence level of 95 percent, to within plus or minus 25 percent for concentrations of AN at or above the permissible exposure limits, and plus or minus 35 percent for concentrations of AN between the action level and the permissible exposure limits.
- (g) Weekly survey of operations involving liquid AN. In addition to monitoring of employee exposures to AN as otherwise required by this subsection, the employer shall survey areas of operations involving liquid AN at least weekly to detect points where AN liquid or vapor are being released into the workplace. The survey shall employ an infra-red gas analyzer calibrated for AN, a multipoint gas chromatographic monitor, or comparable system for detection of AN. A listing of levels detected and areas of AN release, as determined from the survey, shall be posted prominently in the workplace, and shall remain posted until the next survey is completed.

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(6) Regulated areas.

- (a) The employer shall establish regulated areas where AN concentrations are in excess of the permissible exposure limits.
- (b) Regulated areas shall be demarcated and segregated from the rest of the workplace, in any manner that minimizes the number of persons who will be exposed to AN.
- (c) Access to regulated areas shall be limited to authorized persons or to persons otherwise authorized by the act or regulations issued pursuant thereto.
- (d) The employer shall assure that in the regulated area, food or beverages are not present or consumed, smoking products are not present or used, and cosmetics are not applied, (except that these activities may be conducted in the lunchrooms, change rooms and showers required under subsections (13)(a)-(13)(c) of this section.

(7) Methods of compliance.

- (a) Engineering and work-practice controls.
 - (i) The employer shall institute engineering or work-practice controls to reduce and maintain employee exposures to AN, to or below the permissible exposure limits, except to the extent that the employer establishes that such controls are not feasible.
 - (ii) Wherever the engineering and work-practice controls which can be instituted are not sufficient to reduce employee exposures to or below the permissible exposure limits, the employer shall nonetheless use them to reduce exposures to the lowest levels achievable by these controls and shall supplement them by the use of respiratory protection which complies with the requirements of subsection (8) of this section.
- (b) Compliance program.
 - (i) The employer shall establish and implement a written program to reduce employee exposures to or below the permissible exposure limits solely by means of engineering and work-practice controls, as required by subsection (7)(a) of this section.
 - (ii) Written plans for these compliance programs shall include at least the following:
 - (A) A description of each operation or process resulting in employee exposure to AN above the permissible exposure limits;
 - (B) Engineering plans and other studies used to determine the controls for each process;
 - (C) A report of the technology considered in meeting the permissible exposure limits;
 - (D) A detailed schedule for the implementation of engineering or work-practice controls; and
 - (E) Other relevant information.

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- (iii) The employer shall complete the steps set forth in the compliance program by the dates in the schedule.
- (iv) Written plans for such a program shall be submitted upon request to the director, and shall be available at the worksite for examination and copying by the director, or any affected employee or representative.
- (v) The plans required by this subsection shall be revised and updated at least every six months to reflect the current status of the program.

(8) Respiratory protection.

- (a) General. For employees who use respirators required by this section, the employer must provide respirators that comply with the requirements of this subsection. Respirators must be used during:
 - (i) Periods necessary to install or implement feasible engineering and work-practice controls;

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- (ii) Work operations, such as maintenance and repair activities or reactor cleaning, for which the employer establishes that engineering and work-practice controls are not feasible;
- (iii) Work operations for which feasible engineering and work-practice controls are not yet sufficient to reduce employee exposure to or below the permissible exposure limits;
- (iv) Emergencies.
- (b) Respirator program. The employer must implement a respiratory protection program in accordance with chapter 296-842 WAC, except WAC 296-842-13005 and 296-842-14005.
- (c) Respirator selection. The employer must select the appropriate respirator from Table I of this subsection.

TABLE I	
RESPIRATORY PROTECTION FOR ACRYLONITRILE (AN)	
Concentration of AN or Condition of Use	Respirator Type
(a) Less than or equal to 25 x permissible exposure limits.	(i) Any Type C supplied-air respirator
(b) Less than or equal to 100 x permissible exposure limits.	(i) Any supplied-air respirator with full facepiece, or
	(ii) Any self-contained breathing apparatus with full facepiece.
(c) Less than or equal to 250 x permissible exposure limits.	(i) Supplied-air respirator in positive-pressure mode with full facepiece, helmet, hood, or suit.
(d) Greater than 250 x permissible exposure limits.	(i) supplied-air respirator with full facepiece and an auxiliary self-contained air supply, operated in pressure-demand mode; or
	(ii) Open circuit self-contained breathing apparatus with full facepiece in positive-pressure mode.
(e) Emergency entry into unknown concentration or firefighting.	(i) Any self-contained breathing apparatus with full facepiece in positive-pressure mode.
(f) Escape.	(i) Any organic vapor gas mask; or
	(ii) Any self-contained breathing.

(9) Emergency situations.

- (a) Written plans.
 - (i) A written plan for emergency situations shall be developed for each workplace where AN is present. Appropriate portions of the plan shall be implemented in the event of an emergency.
 - (ii) The plan shall specifically provide that employees engaged in correcting emergency conditions shall be equipped as required in subsection (8) of this section until the emergency is abated.

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- (b) Alerting employees.
 - (i) Where there is the possibility of employee exposure to AN in excess of the ceiling limit due to the occurrence of an emergency, a general alarm shall be installed and maintained to promptly alert employees of such occurrences.
 - (ii) Employees not engaged in correcting the emergency shall be evacuated from the area and shall not be permitted to return until the emergency is abated.
- (10) **Protective clothing and equipment.**
 - (a) Provision and use. Where eye or skin contact with liquid AN or PAN may occur, the employer shall provide at no cost to the employee, and assure that employees wear, appropriate protective clothing or other equipment in accordance with WAC 296-800-160 to protect any area of the body which may come in contact with liquid AN or PAN.
 - (b) Cleaning and replacement.
 - (i) The employer shall clean, launder, maintain, or replace protective clothing and equipment required by this subsection, as needed to maintain their effectiveness.

In addition, the employer shall provide clean protective clothing and equipment at least weekly to each affected employee.
 - (ii) The employer shall assure that impermeable protective clothing which contacts or is likely to have contacted liquid AN shall be decontaminated before being removed by the employee.
 - (iii) The employer shall assure that AN- or PAN-contaminated protective clothing and equipment is placed and stored in closable containers which prevent dispersion of the AN or PAN outside the container.
 - (iv) The employer shall assure that an employee whose nonimpermeable clothing becomes wetted with liquid AN shall immediately remove that clothing and proceed to shower. The clothing shall be decontaminated before it is removed from the regulated area.
 - (v) The employer shall assure that no employee removes AN- or PAN-contaminated protective equipment or clothing from the change room, except for those employees authorized to do so for the purpose of laundering, maintenance, or disposal.
 - (vi) The employer shall inform any person who launders or cleans AN-or PAN-contaminated protective clothing or equipment of the potentially harmful effects of exposure to AN.
 - (vii) The employer shall assure that containers of contaminated protective clothing and equipment which are to be removed from the workplace for any reason are labeled in accordance with subsection (16)(c)(ii) of this section, and that such labels remain affixed when such containers leave the employer's workplace.
- (11) **Housekeeping.**
 - (a) All surfaces shall be maintained free of accumulations of liquid AN and of PAN.
 - (b) For operations involving liquid AN, the employer shall institute a program for detecting leaks and spills of liquid AN, including regular visual inspections.

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- (c) Where spills of liquid AN are detected, the employer shall assure that surfaces contacted by the liquid AN are decontaminated. Employees not engaged in decontamination activities shall leave the area of the spill, and shall not be permitted in the area until decontamination is completed.
- (d) Liquids. Where AN is present in a liquid form, or as a resultant vapor, all containers or vessels containing AN shall be enclosed to the maximum extent feasible and tightly covered when not in use, with adequate provision made to avoid any resulting potential explosion hazard.
- (e) Surfaces.
 - (i) Dry sweeping and the use of compressed air for the cleaning of floors and other surfaces where AN and PAN are found is prohibited.
 - (ii) Where vacuuming methods are selected, either portable units or a permanent system may be used.
 - (A) If a portable unit is selected, the exhaust shall be attached to the general workplace exhaust ventilation system or collected within the vacuum unit, equipped with high efficiency filters or other appropriate means of contaminant removal, so that AN is not reintroduced into the workplace air; and
 - (B) Portable vacuum units used to collect AN may not be used for other cleaning purposes and shall be labeled as prescribed by subsection (16)(c)(ii) of this section.
 - (iii) Cleaning of floors and other contaminated surfaces may not be performed by washing down with a hose, unless a fine spray has first been laid down.
- (12) **Waste disposal.** AN and PAN waste, scrap, debris, bags, containers or equipment, shall be disposed of in sealed bags or other closed containers which prevent dispersion of AN outside the container, and labeled as prescribed in subsection (16)(c)(ii) of this section.
- (13) **Hygiene facilities and practices.** Where employees are exposed to airborne concentrations of AN above the permissible exposure limits, or where employees are required to wear protective clothing or equipment pursuant to subsection (11) of this section, or where otherwise found to be appropriate, the facilities required by WAC 296-800-230 shall be provided by the employer for the use of those employees, and the employer shall assure that the employees use the facilities provided. In addition, the following facilities or requirements are mandated.
 - (a) Change rooms. The employer shall provide clean change rooms in accordance with WAC 296-800-230.
 - (b) Showers.
 - (i) The employer shall provide shower facilities in accordance with WAC 296-800-230.
 - (ii) In addition, the employer shall also assure that employees exposed to liquid AN and PAN shower at the end of the work shift.
 - (iii) The employer shall assure that, in the event of skin or eye exposure to liquid AN, the affected employee shall shower immediately to minimize the danger of skin absorption.

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- (c) Lunchrooms.
 - (i) Whenever food or beverages are consumed in the workplace, the employer shall provide lunchroom facilities which have a temperature controlled, positive pressure, filtered air supply, and which are readily accessible to employees exposed to AN above the permissible exposure limits.
 - (ii) In addition, the employer shall also assure that employees exposed to AN above the permissible exposure limits wash their hands and face prior to eating.
- (14) **Medical surveillance.**
 - (a) General.
 - (i) The employer shall institute a program of medical surveillance for each employee who is or will be exposed to AN above the action level. The employer shall provide each such employee with an opportunity for medical examinations and tests in accordance with this subsection.
 - (ii) The employer shall assure that all medical examinations and procedures are performed by or under the supervision of a licensed physician, and shall be provided without cost to the employee.
 - (b) Initial examinations. At the time of initial assignment, or upon institution of the medical surveillance program, the employer shall provide each affected employee an opportunity for a medical examination, including at least the following elements:
 - (i) A work history and medical history with special attention to skin, respiratory, and gastrointestinal systems, and those non-specific symptoms, such as headache, nausea, vomiting, dizziness, weakness, or other central nervous system dysfunctions that may be associated with acute or chronic exposure to AN.
 - (ii) A physical examination giving particular attention to central nervous system, gastrointestinal system, respiratory system, skin and thyroid.
 - (iii) A "14 x 17" posteroanterior chest x-ray.
 - (iv) Further tests of the intestinal tract, including fecal occult blood screening, and proctosigmoidoscopy, for all workers 40 years of age or older, and for any other affected employees for whom, in the opinion of the physician, such testing is appropriate.
 - (c) Periodic examinations.
 - (i) The employer shall provide examinations specified in this subsection at least annually for all employees specified in subsection (14)(a) of this section.
 - (ii) If an employee has not had the examinations prescribed in subsection (14)(b) of this section within six months of termination of employment, the employer shall make such examination available to the employee upon such termination.
 - (d) Additional examinations. If the employee for any reason develops signs or symptoms commonly associated with exposure to AN, the employer shall provide appropriate examination and emergency medical treatment.

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- (e) Information provided to the physician. The employer shall provide the following information to the examining physician:
 - (i) A copy of this standard and its appendices;
 - (ii) A description of the affected employee's duties as they relate to the employee's exposure;
 - (iii) The employee's representative exposure level;
 - (iv) The employee's anticipated or estimated exposure level (for preplacement examinations or in cases of exposure due to an emergency);
 - (v) A description of any personal protective equipment used or to be used; and
 - (vi) Information from previous medical examinations of the affected employee, which is not otherwise available to the examining physician.
 - (f) Physician's written opinion.
 - (i) The employer shall obtain a written opinion from the examining physician which shall include:
 - (A) The results of the medical examination and test performed;
 - (B) The physician's opinion as to whether the employee has any detected medical condition which would place the employee at an increased risk of material impairment of the employee's health from exposure to AN;
 - (C) Any recommended limitations upon the employee's exposure to AN or upon the use of protective clothing and equipment such as respirators; and
 - (D) A statement that the employee has been informed by the physician of the results of the medical examination and any medical conditions which require further examination or treatment.
 - (ii) The employer shall instruct the physician not to reveal in the written opinion specific findings or diagnoses unrelated to occupational exposure to AN.
 - (iii) The employer shall provide a copy of the written opinion to the affected employee.
- (15) **Employee information and training.**
- (a) Training program.
 - (i) The employer shall institute a training program for all employees where there is occupational exposure to AN and shall assure their participation in the training program.
 - (ii) The training program shall be provided at the time of initial assignment, or upon institution of the training program, and at least annually thereafter, and the employer shall assure that each employee is informed of the following:
 - (A) The information contained in Appendices A, B and C;

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- (B) The quantity, location, manner of use, release or storage of AN and the specific nature of operations which could result in exposure to AN, as well as any necessary protective steps;
 - (C) The purpose, proper use, and limitations of respirators and protective clothing;
 - (D) The purpose and a description of the medical surveillance program required by subsection (14) of this section;
 - (E) The emergency procedures developed, as required by subsection (9) of this section; and
 - (F) The engineering and work-practice controls, their function and the employee's relationship thereto; and
 - (G) A review of this standard.
- (b) Access to training materials.
 - (i) The employer shall make a copy of this standard and its appendices readily available to all affected employees.
 - (ii) The employer shall provide, upon request, all materials relating to the employee information and training program to the director.
- (16) **Signs and labels.**
 - (a) General.
 - (i) The employer may use labels or signs required by other statutes, regulations, or ordinances in addition to, or in combination with, signs and labels required by this subsection.
 - (ii) The employer shall assure that no statement appears on or near any sign or label, required by this subsection, which contradicts or detracts from such effects of the required sign or label.
 - (b) Signs.
 - (i) The employer shall post signs to clearly indicate all workplaces where AN concentrations exceed the permissible exposure limits. The signs shall bear the following legend:

DANGER
ACRYLONITRILE (AN)
CANCER HAZARD
AUTHORIZED PERSONNEL ONLY
RESPIRATORS REQUIRED
 - (ii) The employer shall assure that signs required by this subsection are illuminated and cleaned as necessary so that the legend is readily visible.
 - (c) Labels.

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- (i) The employer shall assure that precautionary labels are affixed to all containers of AN, and to containers of PAN and products fabricated from PAN, except for those materials for which objective data is provided as to the conditions specified in subsection (1)(b) of this section. The employer shall assure that the labels remain affixed when the AN or PAN are sold, distributed or otherwise leave the employer's workplace.
- (ii) The employer shall assure that the precautionary labels required by this subsection are readily visible and legible. The labels shall bear the following legend:

**DANGER
CONTAINS ACRYLONITRILE (AN)
CANCER HAZARD**

(17) Recordkeeping.

- (a) Objective data for exempted operations.
 - (i) Where the processing, use, and handling of products fabricated from PAN are exempted pursuant to subsection (1)(b) of this section, the employer shall establish and maintain an accurate record of objective data reasonably relied upon in support of the exemption.
 - (ii) This record shall include the following information:
 - (A) The relevant condition in subsection (1)(b) upon which exemption is based;
 - (B) The source of the objective data;
 - (C) The testing protocol, results of testing, and/or analysis of the material for the release of AN;
 - (D) A description of the operation exempted and how the data supports the exemption; and
 - (E) Other data relevant to the operations, materials, and processing covered by the exemption.
 - (iii) The employer shall maintain this record for the duration of the employer's reliance upon such objective data.
- (b) Exposure monitoring.
 - (i) The employer shall establish and maintain an accurate record of all monitoring required by subsection (5) of this section.
 - (ii) This record shall include:
 - (A) The dates, number, duration, and results of each of the samples taken, including a description of the sampling procedure used to determine representative employee exposure;
 - (B) A description of the sampling and analytical methods used and the data relied upon to establish that the methods used meet the accuracy and precision requirements of subsection (5)(f) of this section;

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- (C) Type of respiratory protective devices worn, if any; and
 - (D) Name, social security number and job classification of the employee monitored and of all other employees whose exposure the measurement is intended to represent.
- (iii) The employer shall maintain this record for at least 40 years or the duration of employment plus 20 years, whichever is longer.
- (c) Medical surveillance.
 - (i) The employer shall establish and maintain an accurate record for each employee subject to medical surveillance as required by subsection (14) of this section.
 - (ii) This record shall include:
 - (A) A copy of the physicians' written opinions;
 - (B) Any employee medical complaints related to exposure to AN;
 - (C) A copy of the information provided to the physician as required by subsection (14)(f) of this section; and
 - (D) A copy of the employee's medical and work history.
 - (iii) The employer shall assure that this record be maintained for at least forty years or for the duration of employment plus twenty years, whichever is longer.
- (d) Availability.
 - (i) The employer shall assure that all records required to be maintained by this section be made available upon request to the director for examination and copying.
 - (ii) Records required by subdivisions (a) through (c) of this subsection shall be provided upon request to employees, designated representatives, and the assistant director in accordance with chapter 296-802 WAC. Records required by subdivision (a) of this section shall be provided in the same manner as exposure monitoring records.
 - (iii) The employer shall assure that employee medical records required to be maintained by this section, be made available, upon request, for examination and copying, to the affected employee or former employee, or to a physician designated by the affected employee, former employee, or designated representative.
- (e) Transfer of records.
 - (i) Whenever the employer ceases to do business, the successor employer shall receive and retain all records required to be maintained by this section.
 - (ii) Whenever the employer ceases to do business and there is no successor employer to receive and retain the records for the prescribed period, these records shall be transmitted to the director.

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- (iii) At the expiration of the retention period for the records required to be maintained pursuant to this section, the employer shall transmit these records to the director.
- (iv) The employer shall also comply with any additional requirements involving transfer of records set forth in chapter 296-802 WAC.

(18) Observation of monitoring.

- (a) Employee observation. The employer shall provide affected employees, or their designated representatives, an opportunity to observe any monitoring of employee exposure to AN conducted pursuant to subsection (5) of this section.
- (b) Observation procedures.
 - (i) Whenever observation of the monitoring of employee exposure to AN requires entry into an area where the use of protective clothing or equipment is required, the employer shall provide the observer with personal protective clothing or equipment required to be worn by employees working in the area, assure the use of such clothing and equipment, and require the observer to comply with all other applicable safety and health procedures.
 - (ii) Without interfering with the monitoring, observers shall be entitled:
 - (A) To receive an explanation of the measurement procedures;
 - (B) To observe all steps related to the measurement of airborne concentrations of AN performed at the place of exposure; and
 - (C) To record the results obtained.

(19) Appendices. The information contained in the appendices is not intended, by itself, to create any additional obligation not otherwise imposed, or to detract from any obligation.

[Statutory Authority: RCW 49.17.010, .040, .050, and .060. 05-03-093 (Order 04-41), § 296-62-07336, filed 01/18/05, effective 03/01/05. Statutory Authority: RCW 49.17.010, .040, .050, and .060. 04-10-026 (Order 03-04) § 296-62-07336, filed 04/27/04, effective 08/01/04. Statutory Authority: RCW 49.17.010, .040, .050, and .060. 03-18-090 (Order 03-15), § 296-62-07336, filed 09/02/03, effective 11/01/03. Statutory Authority: RCW 49.17.010, .040, .050. 01-11-038 (Order 99-36), § 296-62-07336, filed 05/09/01, effective 09/01/01. Statutory Authority: RCW 49.17.010, .040, .050. 99-10 (Order 98-10) § 296-62-07336, filed 05/04/99, effective 09/01/99.] Statutory Authority: Chapter 49.17 RCW. 88-11-021 (Order 88-04), § 296-62-07336, filed 5/11/88.]

WAC 296-62-07337 Appendix A--Substance safety data sheet for acrylonitrile.

(1) Substance identification.

- (a) Substance: Acrylonitrile (CH₂ CHCN).
- (b) Synonyms: Propenenitrile; vinyl cyanide; cyanoethylene; AN; VCN; acylon; carbacryl; fumigrian; ventox.
- (c) Acrylonitrile can be found as a liquid or vapor, and can also be found in polymer resins, rubbers, plastics, polyols, and other polymers having acrylonitrile as a raw or intermediate material.
- (d) AN is used in the manufacture of acrylic and modiacrylic fibers, acrylic plastics and resins, speciality polymers, nitrile rubbers, and other organic chemicals. It has also been used as a fumigant.
- (e) Appearance and odor: Colorless to pale yellow liquid with a pungent odor which can only be detected at concentrations above the permissible exposure level, in a range of 13-19 parts AN per million parts of air (13-19 ppm).
- (f) Permissible exposure: Exposure may not exceed either:

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- (i) Two parts AN per million parts of air (2 ppm) averaged over the eight-hour workday; or
- (ii) Ten parts AN per million parts of air (10 ppm) averaged over any fifteen-minute period in the workday.
- (iii) In addition, skin and eye contact with liquid AN is prohibited.

(2) Health hazard data.

- (a) Acrylonitrile can affect your body if you inhale the vapor (breathing), if it comes in contact with your eyes or skin, or if you swallow it. It may enter your body through your skin.
- (b) Effects of overexposure:
 - (i) Short-term exposure: Acrylonitrile can cause eye irritation, nausea, vomiting, headache, sneezing, weakness, and light-headedness. At high concentrations, the effects of exposure may go on to loss of consciousness and death. When acrylonitrile is held in contact with the skin after being absorbed into shoe leather or clothing, it may produce blisters following several hours of no apparent effect. Unless the shoes or clothing are removed immediately and the area washed, blistering will occur. Usually there is no pain or inflammation associated with blister formation.
 - (ii) Long-term exposure: Acrylonitrile has been shown to cause cancer in laboratory animals and has been associated with higher incidences of cancer in humans. Repeated or prolonged exposure of the skin to acrylonitrile may produce irritation and dermatitis.
 - (iii) Reporting signs and symptoms: You should inform your employer if you develop any signs or symptoms and suspect they are caused by exposure to acrylonitrile.

(3) Emergency first aid procedures.

- (a) Eye exposure: If acrylonitrile gets into your eyes, wash your eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
- (b) Skin exposure: If acrylonitrile gets on your skin, immediately wash the contaminated skin with water. If acrylonitrile soaks through your clothing, especially your shoes, remove the clothing immediately and wash the skin with water. If symptoms occur after washing, get medical attention immediately. Thoroughly wash the clothing before reusing. Contaminated leather shoes or other leather articles should be discarded.
- (c) Inhalation: If you or any other person breathes in large amounts of acrylonitrile, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
- (d) Swallowing: When acrylonitrile has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
- (e) Rescue: Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency procedures. Do not become a casualty yourself. Understand your emergency rescue procedures and know the location of the emergency equipment before the need arises.

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- (f) Special first aid procedures: First aid kits containing an adequate supply (at least two dozen) of amyl nitrite pearls, each containing 0.3 ml, should be maintained at each site where acrylonitrile is used. When a person is suspected of receiving an overexposure to acrylonitrile, immediately remove that person from the contaminated area using established rescue procedures. Contaminated clothing must be removed and the acrylonitrile washed from the skin immediately. Artificial respiration should be started at once if breathing has stopped. If the person is unconscious, amyl nitrite may be used as an antidote by a properly trained individual in accordance with established emergency procedures. Medical aid should be obtained immediately.
- (4) **Respirators and protective clothing.**
- (a) Respirators: You may be required to wear a respirator for nonroutine activities, in emergencies, while your employer is in the process of reducing acrylonitrile exposures through engineering controls, and in areas where engineering controls are not feasible. If respirators are worn, they must have a label issued by the National Institute for Occupational Safety and Health under the provisions of 42 CFR part 84 stating that the respirators have been certified for use with organic vapors. For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work situations where their use is required.
 - (b) Supplied-air suits: In some work situations, the wearing of supplied-air suits may be necessary. Your employer must instruct you in their proper use and operation.
 - (c) Protective clothing:
 - (i) You must wear impervious clothing, gloves, face shield, or other appropriate protective clothing to prevent skin contact with liquid acrylonitrile. Where protective clothing is required, your employer is required to provide clean garments to you as necessary to assume that the clothing protects you adequately.
 - (ii) Replace or repair impervious clothing that has developed leaks.
 - (iii) Acrylonitrile should never be allowed to remain on the skin. Clothing and shoes which are not impervious to acrylonitrile should not be allowed to become contaminated with acrylonitrile, and if they do the clothing and shoes should be promptly removed and decontaminated. The clothing should be laundered or discarded after the AN is removed. Once acrylonitrile penetrates shoes or other leather articles, they should not be worn again.
 - (d) Eye protection: You must wear splashproof safety goggles in areas where liquid acrylonitrile may contact your eyes. In addition, contact lenses should not be worn in areas where eye contact with acrylonitrile can occur.
- (5) **Precautions for safe use, handling, and storage.**
- (a) Acrylonitrile is a flammable liquid, and its vapors can easily form explosive mixtures in air.
 - (b) Acrylonitrile must be stored in tightly closed containers in a cool, well-ventilated area, away from heat, sparks, flames, strong oxidizers (especially bromine), strong bases, copper, copper alloys, ammonia, and amines.
 - (c) Sources of ignition such as smoking and open flames are prohibited wherever acrylonitrile is handled, used, or stored in a manner that could create a potential fire or explosion hazard.

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- (d) You should use nonsparking tools when opening or closing metal containers of acrylonitrile, and containers must be bonded and grounded when pouring or transferring liquid acrylonitrile.
- (e) You must immediately remove any nonimpervious clothing that becomes wetted with acrylonitrile, and this clothing must not be reworn until the acrylonitrile is removed from the clothing.
- (f) Impervious clothing wet with liquid acrylonitrile can be easily ignited. This clothing must be washed down with water before you remove it.
- (g) If your skin becomes wet with liquid acrylonitrile, you must promptly and thoroughly wash or shower with soap or mild detergent to remove any acrylonitrile from your skin.
- (h) You must not keep food, beverages, or smoking materials, nor are you permitted to eat or smoke in regulated areas where acrylonitrile concentrations are above the permissible exposure limits.
- (i) If you contact liquid acrylonitrile, you must wash your hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- (j) Fire extinguishers and quick drenching facilities must be readily available, and you should know where they are and how to operate them.
- (k) Ask your supervisor where acrylonitrile is used in your work area and for any additional plant safety and health rules.

(6) Access to information.

- (a) Each year, your employer is required to inform you of the information contained in this Substance Safety Data Sheet for acrylonitrile. In addition, your employer must instruct you in the proper work-practices for using acrylonitrile, emergency procedures, and the correct use of protective equipment.
- (b) Your employer is required to determine whether you are being exposed to acrylonitrile. You or your representative has the right to observe employee measurements and to record the results obtained. Your employer is required to inform you of your exposure. If your employer determines that you are being overexposed, he or she is required to inform you of the actions which are being taken to reduce your exposure to within permissible exposure limits.
- (c) Your employer is required to keep records of your exposures and medical examinations. These records must be kept by the employer for at least forty years or for the period of your employment plus twenty years, whichever is longer.
- (d) Your employer is required to release your exposure and medical records to you or your representative upon your request.

[Statutory Authority: RCW 49.17.010, .040, .050. 99-10 (Order 98-10) § 296-62-07337, filed 05/04/99, effective 09/01/99.] Statutory Authority: Chapter 49.17 RCW. 94-15-096 (Order 94-07), § 296-62-07337, filed 7/20/94, effective 9/20/94; 88-11-021 (Order 88-04), § 296-62-07337, filed 5/11/88.]

WAC 296-62-07338 Appendix B--Substance technical guidelines for acrylonitrile.

(1) Physical and chemical data.

- (a) Substance identification:
 - (i) Synonyms: AN; VCN; vinyl cyanide; propenenitrile; cyanoethylene; Acrylon; Carbacryl; Fumigrain; Ventox.

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- (ii) Formula: $\text{CH}_2 = \text{CHCN}$.
 - (iii) Molecular weight: 53.1.
- (b) Physical data:
 - (i) Boiling point (760 mm Hg): 77.3°C (171°F);
 - (ii) Specific gravity (water = 1): 0.81 (at 20°C or 68°F);
 - (iii) Vapor density (air = 1 at boiling point of acrylonitrile): 1.83;
 - (iv) Melting point: -83°C (-117°F);
 - (v) Vapor pressure (@20°F): 83 mm Hg;
 - (vi) Solubility in water, percent by weight @20°C (68°F): 7.35;
 - (vii) Evaporation rate (Butyl Acetate = 1): 4.54; and
 - (viii) Appearance and odor: Colorless to pale yellow liquid with a pungent odor at concentrations above the permissible exposure level. Any detectable odor of acrylonitrile may indicate overexposure.
- (2) **Fire, explosion, and reactivity hazard data.**
 - (a) Fire:
 - (i) Flash point: -1°C (30°F) (closed cup).
 - (ii) Autoignition temperature: 481°C (898°F).
 - (iii) Flammable limits air, percent by volume: Lower: 3, Upper: 17.
 - (iv) Extinguishing media: Alcohol foam, carbon dioxide, and dry chemical.
 - (v) Special fire-fighting procedures: Do not use a solid stream of water, since the stream will scatter and spread the fire. Use water to cool containers exposed to a fire.
 - (vi) Unusual fire and explosion hazards: Acrylonitrile is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where acrylonitrile is handled, used, or stored in a manner that could create a potential fire or explosion hazard. Acrylonitrile vapors are heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which acrylonitrile is being handled.
 - (vii) For purposes of compliance with the requirements of WAC 296-800-300, acrylonitrile is classified as a Class IB flammable liquid. For example, 7,500 ppm, approximately one-fourth of the lower flammable limit, would be considered to pose a potential fire and explosion hazard.
 - (viii) For purposes of compliance with WAC 296-24-59207, acrylonitrile is classified as a Class B fire hazard.

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- (ix) For purpose of compliance with WAC 296-24-95613, locations classified as hazardous due to the presence of acrylonitrile shall be Class I, Group D.
- (b) Reactivity:
 - (i) Conditions contributing to instability: Acrylonitrile will polymerize when hot, and the additional heat liberated by the polymerization may cause containers to explode. Pure AN may self-polymerize, with a rapid build-up of pressure, resulting in an explosion hazard. Inhibitors are added to the commercial product to prevent self-polymerization.
 - (ii) Incompatibilities: Contact with strong oxidizers (especially bromine) and strong bases may cause fires and explosions. Contact with copper, copper alloys, ammonia, and amines may start serious decomposition.
 - (iii) Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving acrylonitrile and certain polymers made from acrylonitrile.
 - (iv) Special precautions: Liquid acrylonitrile will attack some forms of plastics, rubbers, and coatings.
- (3) **Spill, leak, and disposal procedures.**
 - (a) If acrylonitrile is spilled or leaked, the following steps should be taken:
 - (i) Remove all ignition sources.
 - (ii) The area should be evacuated at once and re-entered only after the area has been thoroughly ventilated and washed down with water.
 - (iii) If liquid acrylonitrile or polymer intermediate, collect for reclamation or absorb in paper, vermiculite, dry sand, earth, or similar material, or wash down with water into process sewer system.
 - (b) Persons not wearing protective equipment should be restricted from areas of spills or leaks until clean-up has been completed.
 - (c) Waste disposal methods: Waste materials shall be disposed of in a manner that is not hazardous to employees or to the general population. Spills of acrylonitrile and flushing of such spills shall be channeled for appropriate treatment or collection for disposal. They shall not be channeled directly into the sanitary sewer system. In selecting the method of waste disposal, applicable local, state, and federal regulations should be consulted.
- (4) **Monitoring and measurement procedures.**
 - (a) Exposure above the permissible exposure limit:
 - (i) Eight-hour exposure evaluation: Measurements taken for the purpose of determining employee exposure under this section are best taken so that the average eight-hour exposure may be determined from a single eight-hour sample or two four-hour samples.

Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

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- (ii) Ceiling evaluation: Measurements taken for the purpose of determining employee exposure under this section must be taken during periods of maximum expected airborne concentrations of acrylonitrile in the employee's breathing zone. A minimum of three measurements should be taken on one work shift. The average of all measurements taken is an estimate of the employee's ceiling exposure.
 - (iii) Monitoring techniques: The sampling and analysis under this section may be performed by collecting the acrylonitrile vapor on charcoal adsorption tubes or other composition adsorption tubes, with subsequent chemical analysis. Sampling and analysis may also be performed by instruments such as real-time continuous monitoring systems, portable direct-reading instruments, or passive dosimeters. Analysis of resultant samples should be by gas chromatograph.
 - (iv) Appendix D lists methods of sampling and analysis which have been tested by NIOSH and OSHA for use with acrylonitrile. NIOSH and OSHA have validated modifications of NIOSH Method S-156 (see Appendix D) under laboratory conditions for concentrations below 1 ppm. The employer has the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the standard under his/her unique field conditions. The standard requires that methods of monitoring must be accurate, to a 95-percent confidence level, to ± 35 -percent for concentrations of AN at or above 2 ppm, and to ± 50 -percent for concentrations below 2 ppm. In addition to the methods described in Appendix D, there are numerous other methods available for monitoring for AN in the workplace. Details on these other methods have been submitted by various companies to the rulemaking record, and are available at the OSHA Docket Office.
 - (b) Since many of the duties relating to employee exposure are dependent on the results of monitoring and measuring procedures, employers shall assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.
- (5) **Protective clothing.**
- (a) Employees shall be provided with and required to wear appropriate protective clothing to prevent any possibility of skin contact with liquid AN. Because acrylonitrile is absorbed through the skin, it is important to prevent skin contact with liquid AN. Protective clothing shall include impermeable coveralls or similar full-body work clothing, gloves, head-coverings, as appropriate to protect areas of the body which may come in contact with liquid AN.
 - (b) Employers should ascertain that the protective garments are impermeable to acrylonitrile. Nonimpermeable clothing and shoes should not be allowed to become contaminated with liquid AN. If permeable clothing does become contaminated, it should be promptly removed, placed in a regulated area for removal of the AN, and not worn again until the AN is removed. If leather footwear or other leather garments become wet from acrylonitrile, they should be replaced and not worn again, due to the ability of leather to absorb acrylonitrile and hold it against the skin. Since there is no pain associated with the blistering which may result from skin contact with liquid AN, it is essential that the employee be informed of this hazard so that he or she can be protected.
 - (c) Any protective clothing which has developed leaks or is otherwise found to be defective shall be repaired or replaced. Clean protective clothing shall be provided to the employee as necessary to assure its protectiveness. Whenever impervious clothing becomes wet with liquid AN, it shall be washed down with water before being removed by the employee. Employees are also required to wear splash-proof safety goggles where there is any possibility of acrylonitrile contacting the eyes.
- (6) **Housekeeping and hygiene facilities.** For purposes of complying with WAC 296-24-120, 296-800-220 and 296-800-230, the following items should be emphasized:

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- (a) The workplace should be kept clean, orderly, and in a sanitary condition. The employer is required to institute a leak and spill detection program for operations involving liquid AN in order to detect sources of fugitive AN emissions.
 - (b) Dry sweeping and the use of compressed air is unsafe for the cleaning of floors and other surfaces where liquid AN may be found.
 - (c) Adequate washing facilities with hot and cold water are to be provided, and maintained in a sanitary condition. Suitable cleansing agents are also to be provided to assure the effective removal of acrylonitrile from the skin.
 - (d) Change or dressing rooms with individual clothes storage facilities must be provided to prevent the contamination of street clothes with acrylonitrile. Because of the hazardous nature of acrylonitrile, contaminated protective clothing should be placed in a regulated area designated by the employer for removal of the AN before the clothing is laundered or disposed of.
- (7) **Miscellaneous precautions.**
- (a) Store acrylonitrile in tightly-closed containers in a cool, well-ventilated area and take necessary precautions to avoid any explosion hazard.
 - (b) High exposures to acrylonitrile can occur when transferring the liquid from one container to another.
 - (c) Nonsparking tools must be used to open and close metal acrylonitrile containers. These containers must be effectively grounded and bonded prior to pouring.
 - (d) Never store uninhibited acrylonitrile.
 - (e) Acrylonitrile vapors are not inhibited.
They may form polymers and clog vents of storage tanks.
 - (f) Use of supplied-air suits or other impervious coverings may be necessary to prevent skin contact with and provide respiratory protection from acrylonitrile where the concentration of acrylonitrile is unknown or is above the ceiling limit. Supplied-air suits should be selected, used, and maintained under the immediate supervision of persons knowledgeable in the limitations and potential life-endangering characteristics of supplied-air suits.
 - (g) Employers shall advise employees of all areas and operations where exposure to acrylonitrile could occur.
- (8) **Common operations.** Common operations in which exposure to acrylonitrile is likely to occur include the following: Manufacture of the acrylonitrile monomer; synthesis of acrylic fibers, ABS, SAN, and nitrile barrier plastics and resins, nitrile rubber, surface coatings, specialty chemicals; use as a chemical intermediate; use as a fumigant; and in the cyanoethylation of cotton.

[Statutory Authority: RCW 49.17.010, .040, .050. 01-11-038 (Order 99-36), § 296-62-07338, filed 05/09/01, effective 09/01/01.
Statutory Authority: Chapter 49.17 RCW. 88-11-021 (Order 88-04), § 296-62-07338, filed 5/11/88.]

WAC 296-62-07339 Appendix C--Medical surveillance guidelines for acrylonitrile.

- (1) **Route of entry.**
- (a) Inhalation;

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- (b) Skin absorption;
 - (c) Ingestion.
- (2) **Toxicology.**
- (a) Acrylonitrile vapor is an asphyxiant due to inhibitory action on metabolic enzyme systems. Animals exposed to 75 or 100 ppm for seven hours have shown signs of anoxia; in some animals which died at the higher level, cyanomethemoglobin was found in the blood. Two human fatalities from accidental poisoning have been reported; one was caused by inhalation of an unknown concentration of the vapor, and the other was thought to be caused by skin absorption or inhalation. Most cases of intoxication from industrial exposure have been mild, with rapid onset of eye irritation, headache, sneezing, and nausea. Weakness, lightheadedness, and vomiting may also occur. Exposure to high concentrations may produce profound weakness, asphyxia, and death. The vapor is a severe eye irritant. Prolonged skin contact with the liquid may result in absorption with systemic effects, and in the formation of large blisters after a latent period of several hours. Although there is usually little or no pain or inflammation, the affected skin resembles a second-degree thermal burn. Solutions spilled on exposed skin, or on areas covered only by a light layer of clothing, evaporate rapidly, leaving no irritation, or, at the most, mild transient redness. Repeated spills on exposed skin may result in dermatitis due to solvent effects.
 - (b) Results after one year of a planned two-year animal study on the effects of exposure to acrylonitrile have indicated that rats ingesting as little as 35 ppm in their drinking water develop tumors of the central nervous system. The interim results of this study have been supported by a similar study being conducted by the same laboratory, involving exposure of rats by inhalation of acrylonitrile vapor, which has shown similar types of tumors in animals exposed to 80 ppm.
 - (c) In addition, the preliminary results of an epidemiological study being performed by duPont on a cohort of workers in their Camden, S.C. acrylic fiber plant indicate a statistically significant increase in the incidence of colon and lung cancers among employees exposed to acrylonitrile.
- (3) **Signs and symptoms of acute overexposure.** Asphyxia and death can occur from exposure to high concentrations of acrylonitrile. Symptoms of overexposure include eye irritation, headache, sneezing, nausea and vomiting, weakness, and light-headedness. Prolonged skin contact can cause blisters on the skin with appearance of a second-degree burn, but with little or no pain. Repeated skin contact may produce scaling dermatitis.
- (4) **Treatment of acute overexposure.** Remove employee from exposure. Immediately flush eyes with water and wash skin with soap or mild detergent and water. If AN has been swallowed, and person is conscious, induce vomiting. Give artificial respiration if indicated. More severe cases, such as those associated with loss of consciousness, may be treated by the intravenous administration of sodium nitrite, followed by sodium thiosulfate, although this is not as effective for acrylonitrile poisoning as for inorganic cyanide poisoning.
- (5) **Surveillance and preventive considerations.**
- (a) As noted above, exposure to acrylonitrile has been linked to increased incidence of cancers of the colon and lung in employees of the duPont acrylic fiber plant in Camden, S.C. In addition, the animal testing of acrylonitrile has resulted in the development of cancers of the central nervous system in rats exposed by either inhalation or ingestion. The physician should be aware of the findings of these studies in evaluating the health of employees exposed to acrylonitrile.

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- (b) Most reported acute effects of occupational exposure to acrylonitrile are due to its ability to cause tissue anoxia and asphyxia. The effects are similar to those caused by hydrogen cyanide. Liquid acrylonitrile can be absorbed through the skin upon prolonged contact. The liquid readily penetrates leather, and will produce burns of the feet if footwear contaminated with acrylonitrile is not removed.
- (c) It is important for the physician to become familiar with the operating conditions in which exposure to acrylonitrile may occur. Those employees with skin diseases may not tolerate the wearing of whatever protective clothing may be necessary to protect them from exposure. In addition, those with chronic respiratory disease may not tolerate the wearing of negative-pressure respirators.
- (d) Surveillance and screening. Medical histories and laboratory examinations are required for each employee subject to exposure to acrylonitrile above the action level. The employer must screen employees for history of certain medical conditions which might place the employee at increased risk from exposure.
 - (i) Central nervous system dysfunction. Acute effects of exposure to acrylonitrile generally involve the central nervous system. Symptoms of acrylonitrile exposure include headache, nausea, dizziness, and general weakness. The animal studies cited above suggest possible carcinogenic effects of acrylonitrile on the central nervous system, since rats exposed by either inhalation or ingestion have developed similar CNS tumors.
 - (ii) Respiratory disease. The duPont data indicate an increased risk of lung cancer among employees exposed to acrylonitrile.
 - (iii) Gastrointestinal disease. The duPont data indicate an increased risk of cancer of the colon among employees exposed to acrylonitrile. In addition, the animal studies show possible tumor production in the stomachs of the rats in the ingestion study.
 - (iv) Skin disease. Acrylonitrile can cause skin burns when prolonged skin contact with the liquid occurs. In addition, repeated skin contact with the liquid can cause dermatitis.
- (e) General. The purpose of the medical procedures outlined in the standard is to establish a baseline for future health monitoring. Persons unusually susceptible to the effects of anoxia or those with anemia would be expected to be at increased risk. In addition to emphasis on the CNS, respiratory and gastro-intestinal systems, the cardiovascular system, liver, and kidney function should also be stressed.

[Statutory Authority: Chapter 49.17 RCW. 88-11-021 (Order 88-04), § 296-62-07339, filed 5/11/88.]

WAC 296-62-07340 Appendix D--Sampling and analytical methods for acrylonitrile.

- (1) There are many methods available for monitoring employee exposures to acrylonitrile. Most of these involve the use of charcoal tubes and sampling pumps, with analysis by gas chromatograph. The essential differences between the charcoal tube methods include, among others, the use of different desorbing solvents, the use of different lots of charcoal, and the use of different equipment for analysis of the samples.
- (2) Besides charcoal, considerable work has been performed on methods using porous polymer sampling tubes and passive dosimeters. In addition, there are several portable gas analyzers and monitoring units available on the open market.
- (3) This appendix contains details for the methods which have been tested at OSHA Analytical Laboratory in Salt Lake City, and NIOSH in Cincinnati. Each is a variation on NIOSH Method S-156, which is also included for reference. This does not indicate that these methods are the only ones which will be

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satisfactory. There also may be workplace situations in which these methods are not adequate, due to such factors as high humidity. Copies of the other methods available to OSHA are available in the rulemaking record, and may be obtained from the OSHA docket office. These include, the Union Carbide, Monsanto, Dow Chemical and Dow Badische methods, as well as NIOSH Method P & CAM 127.

- (4) Employers who note problems with sample breakthrough should try larger charcoal tubes. Tubes of larger capacity are available, and are often used for sampling vinyl chloride. In addition, lower flow rates and shorter sampling times should be beneficial in minimizing breakthrough problems.
- (5) Whatever method the employer chooses, he must assure himself of the method's accuracy and precision under the unique conditions present in his workplace.
- (6) NIOSH Method S-156 (unmodified)

Analyte: Acrylonitrile.

Matrix: Air.

Procedure: Absorption on charcoal, desorption with methanol, GC.

- (a) Principle of the method. Reference (k)(i) of this subsection.
 - (i) A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
 - (ii) The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with methanol.
 - (iii) An aliquot of the desorbed sample is injected into a gas chromatograph.
 - (iv) The area of the resulting peak is determined and compared with areas obtained for standards.
- (b) Range and sensitivity.
 - (i) This method was validated over the range of 17.5-70.0 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a twenty-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 4.5-135 mg/cu m. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
 - (ii) The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of acrylonitrile and other substances in the air. The first section of the charcoal tube was found to hold at least 3.97 mg of acrylonitrile when a test atmosphere containing 92.0 mg/cu m of acrylonitrile in air was sampled 0.18 liter per minute for 240 minutes; at that time the concentration of acrylonitrile in the effluent was less than 5 percent of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam.) See (f)(ii) of this subsection. If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

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- (c) Interference.
 - (i) When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
 - (ii) When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
 - (iii) It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
 - (iv) If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.
- (d) Precision and accuracy.
 - (i) The coefficient of variation (CVt) for the total analytical and sampling method in the range of 17.5-70.0 mg/cu m was 0.073. This value corresponds to a 3.3 mg/cu m standard deviation at the (previous) OSHA standard level (20 ppm). Statistical information and details of the validation and experimental test procedures can be found in (k)(ii) of this subsection.
 - (ii) On the average the concentrations obtained at the 20 ppm level using the overall sampling and analytical method were 6.0 percent lower than the “true” concentrations for a limited number of laboratory experiments. Any difference between the “found” and “true” concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined “true” concentration. Therefore, no recovery correction should be applied to the final result in (j)(v) of this subsection.
- (e) Advantages and disadvantages of the method.
 - (i) The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.
 - (ii) The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions.
 - (iii) One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25 percent of that found on the front section, the possibility of sample loss exists.
 - (iv) Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

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- (f) Apparatus.
 - (i) A calibrated personal sampling pump whose flow can be determined within ± 5 percent at the recommended flow rate. Reference (k)(iii) of this subsection.
 - (ii) Charcoal tubes: Glass tubes with both ends flame sealed, 7 cm long with a 6 mm O.D. and a 4 mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3 mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silicated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.
 - (iii) Gas chromatograph equipped with a flame ionization detector.
 - (iv) Column (4 ft x 1/4 in stainless steel) packed with 50/80 mesh Poropak, type Q.
 - (v) An electronic integrator or some other suitable method for measuring peak areas.
 - (vi) Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
 - (vii) Microliter syringes: Ten-microliter and other convenient sizes for making standards.
 - (viii) Pipets: 1.0 ml delivery pipets.
 - (ix) Volumetric flask: 10 ml or convenient sizes for making standard solutions.
- (g) Reagents.
 - (i) Chromatographic quality methanol.
 - (ii) Acrylonitrile, reagent grade.
 - (iii) Hexane, reagent grade.
 - (iv) Purified nitrogen.
 - (v) Prepurified hydrogen.
 - (vi) Filtered compressed air.
- (h) Procedure.
 - (i) Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - (ii) Calibration of personal pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - (iii) Collection and shipping of samples.

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- (A) Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2mm).
 - (B) The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.
 - (C) The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - (D) Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - (E) A maximum sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least ± 5 percent.
 - (F) The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
 - (G) The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
 - (H) With each batch of ten samples submit one tube from the same lot of tubes which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.
 - (I) Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
 - (J) A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.
- (iv) Analysis of samples.
- (A) Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2 ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
 - (B) Desorption of samples. Prior to analysis, 1.0 ml of methanol is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.
 - (C) GC conditions. The typical operating conditions for the gas chromatograph are:
 - (I) 50 ml/min (60 psig) nitrogen carrier gas flow.
 - (II) 65 ml/min (24 psig) hydrogen gas flow to detector.

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- (III) 500 ml/min (50 psig) air flow to detector.
- (IV) 235°C injector temperature.
- (V) 255°C manifold temperature (detector).
- (VI) 155°C column temperature.
- (D) Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a five microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3 percent difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.
- (E) Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- (v) Determination of desorption efficiency.
 - (A) Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
 - (B) Procedure for determining desorption efficiency.
 - (I) Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in., 4 mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of acrylonitrile containing 0.239 g/ml is injected directly into the activated charcoal with a microliter syringe, and tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tube.
 - (II) The amount injected is equivalent to that present in a twenty-liter air sample at the selected level.

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- (III) Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the sample. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in (h)(iv) of this subsection.
- (IV) Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.
- (V) The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average weight recovered (mg)}}{\text{weight added (mg)}}$$

- (VI) The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in (j)(iv) of this subsection to correct for adsorption losses.
- (i) Calibration and standards. It is convenient to express concentration of standards in terms of mg/1.0 ml methanol, because samples are desorbed in this amount of methanol. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area.

Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

- (j) Calculations.
 - (i) Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml methanol and the volume of sample injected is identical to the volume of the standards injected.
 - (ii) Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

Where:

$$\text{mg sample} = \text{mg found in front section of sample tube.}$$

$$\text{mg sample} = \text{mg found in front section of blank tube.}$$

Note: A similar procedure is followed for the backup sections.

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- (iii) Add the weights found in the front and backup sections to get the total weight in the sample.
- (iv) Read the desorption efficiency from the curve (reference (h)(v)(B) of this subsection) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

- (v) The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \text{Corrected mg (see (j)(iv))} \times \frac{1,000 \text{ (liter/cu m)}}{\text{air volume sampled (liter)}}$$

- (vi) Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times 24.45/\text{M.W.} \times 760/\text{P} \times \text{T} + 273/298$$

Where:

P = Pressure (mm Hg) of air sampled.

T = Temperature (°C) of air sampled.

24.45 = Molar volume (liter/mole) at 25°C and 760 mm Hg.

M.W. = Molecular weight (g/mole) of analyte.

760 = Standard pressure (mm Hg).

298 = Standard temperature (°K).

- (k) References.
 - (i) White, L. D. et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31:225 (1970).
 - (ii) Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
 - (iii) Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.
- (7) NIOSH Modification of NIOSH Method S-156. The NIOSH recommended method for low levels for acrylonitrile is a modification of method S-156. It differs in the following respects:
 - (a) Samples are desorbed using 1 ml of 1 percent acetone in CS₂ rather than methanol.
 - (b) The analytical column and conditions are:

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- (i) Column: 20 percent SP-1000 on 80/100 Supelcoport 10 feet x 1/8 inch S.S.
 - (ii) Conditions:
 - Injector temperature: 200°C.
 - Detector temperature: 100°C.
 - Column temperature: 85°C.
 - Helium flow: 25 ml/min.
 - Air flow: 450 ml/min.
 - Hydrogen flow: 55 ml/min.
 - (c) A 2 µl injection of the desorbed analyte is used.
 - (d) A sampling rate of 100 ml/min is recommended.
- (8) OSHA Laboratory Modification of NIOSH Method S-156.
 - (a) Analyte: Acrylonitrile.
 - (b) Matrix: Air.
 - (c) Procedure: Adsorption on charcoal, desorption with methanol, GC.
 - (d) Principle of the method (subsection (1)(a) of this section).
 - (i) A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
 - (ii) The charcoal in the tube is transferred to a small, stoppered sample vial, and the analyte is desorbed with methanol.
 - (iii) An aliquot of the desorbed sample is injected into a gas chromatograph.
 - (iv) The area of the resulting peak is determined and compared with areas obtained for standards.
 - (e) Advantages and disadvantages of the method.
 - (i) The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.
 - (ii) This method may not be adequate for the simultaneous analysis of two or more substances.

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- (iii) The amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25 percent of that found on the front section, the possibility of sample loss exists.
 - (iv) The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.
- (f) Apparatus.
 - (i) A calibrated personal sampling pump whose flow can be determined within ± 5 percent at the recommended flow rate.
 - (ii) Charcoal tubes: Glass tube with both ends flame sealed, 7 cm long with a 6 mm O.D. and a 4 mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the back-up section 50 mg. A 3 mm portion of urethane foam is placed between the outlet end of the tube and the back-up section. A plug of silicated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
 - (iii) Gas chromatograph equipped with a nitrogen phosphorus detector.
 - (iv) Column (10 ft x 1/8 in stainless steel) packed with 100/120 Supelcoport coated with 10 percent SP 1000.
 - (v) An electronic integrator or some other suitable method for measuring peak area.
 - (vi) Two-milliliter sample vials with Teflon-lined caps.
 - (vii) Microliter syringes: 10 microliter, and other convenient sizes for making standards.
 - (viii) Pipets: 1.0 ml delivery pipets.
 - (ix) Volumetric flasks: Convenient sizes for making standard solutions.
- (g) Reagents.
 - (i) Chromatographic quality methanol.
 - (ii) Acrylonitrile, reagent grade.
 - (iii) Filtered compressed air.
 - (iv) Purified hydrogen.
 - (v) Purified helium.
- (h) Procedure.
 - (i) Cleaning of equipment. All glassware used for the laboratory analysis should be properly cleaned and free of organics which could interfere in the analysis.

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- (ii) Calibration of personal pumps. Each pump must be calibrated with a representative charcoal tube in the line.
- (iii) Collection and shipping of samples.
 - (A) Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - (B) The smaller section of the charcoal is used as the backup and should be placed nearest the sampling pump.
 - (C) The charcoal should be placed in a vertical position during sampling to minimize channeling through the charcoal.
 - (D) Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - (E) A sample size of 20 liters is recommended. Sample at a flow rate of approximately 0.2 liters per minute. The flow rate should be known with an accuracy of at least ± 5 percent.
 - (F) The temperature and pressure of the atmosphere being sampled should be recorded.
 - (G) The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Rubber caps should not be used.
 - (H) Submit at least one blank tube (a charcoal tube subjected to the same handling procedures, without having any air drawn through it) with each set of samples.
 - (I) Take necessary shipping and packing precautions to minimize breakage of samples.
- (iv) Analysis of samples.
 - (A) Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2 ml vial. The separating section of foam is removed and discarded; the section is transferred to another capped vial. These two sections are analyzed separately.
 - (B) Desorption of samples. Prior to analysis, 1.0 ml of methanol is pipetted into each sample container. Desorption should be done for 30 minutes in an ultrasonic bath. The sample vials are recapped as soon as the solvent is added.
 - (C) GC conditions. The typical operating conditions for the gas chromatograph are:
 - (I) 30 ml/min (60 psig) helium carrier gas flow.
 - (II) 3.0 ml/min (30 psig) hydrogen gas flow to detector.
 - (III) 50 ml/min (60 psig) air flow to detector.

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- (IV) 200°C injector temperature.
 - (V) 200°C dejector temperature.
 - (VI) 100°C column temperature.
 - (D) Injection. Solvent flush technique or equivalent.
 - (E) Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
 - (v) Determination of desorption efficiency.
 - (A) Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine, at least once, the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
 - (B) Procedure for determining desorption efficiency. The reference portion of the charcoal tube is removed. To the remaining portion, amounts representing 0.5X, 1X, and 2X (X represents TLV) based on a 20 l air sample are injected onto several tubes at each level. Dilutions of acrylonitrile with methanol are made to allow injection of measurable quantities. These tubes are then allowed to equilibrate at least overnight. Following equilibration they are analyzed following the same procedure as the samples. A curve of the desorption efficiency (amt recovered/amt added) is plotted versus amount of analyte found. This curve is used to correct for adsorption losses.
 - (i) Calibration and standards. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are prepared by plotting concentration versus peak area.
- Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the NPD response. Multiple injections are necessary.*
- (j) Calculations. Read the weight, corresponding to each peak area from the standard curve, correct for the blank, correct for the desorption efficiency, and make necessary air volume corrections.
 - (k) Reference. NIOSH Method S-156.

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